Rate theory – applications and comparison with experiments
(Barbu3)

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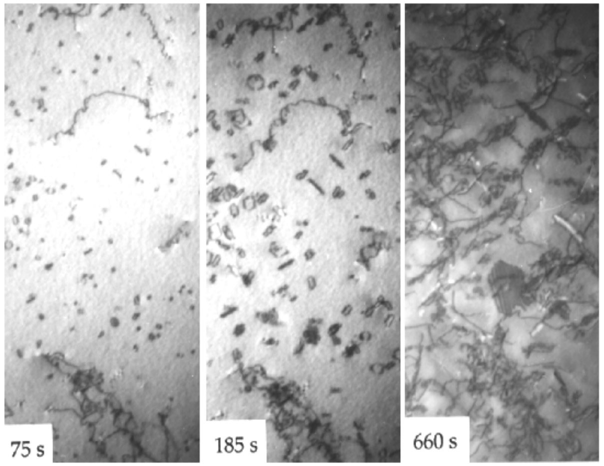
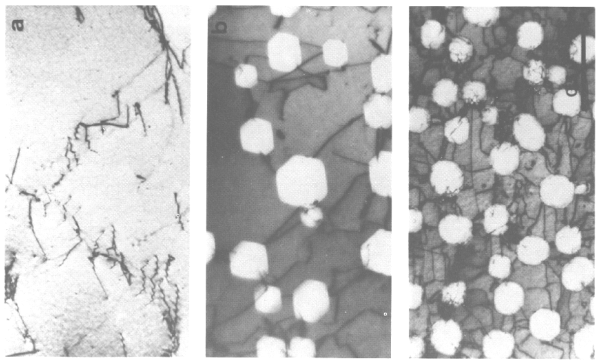
Microstructural evolution under irradiation

Point defects evolution



⇨ Dislocation network

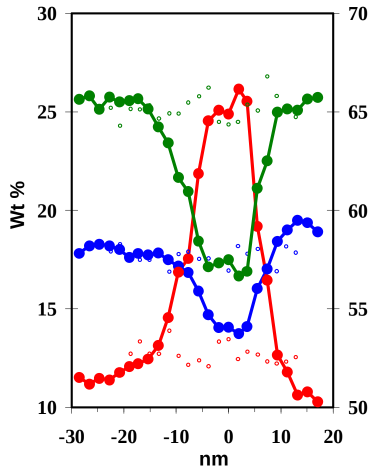
Nucleation and growth of dislocation loops
Dislocation climb



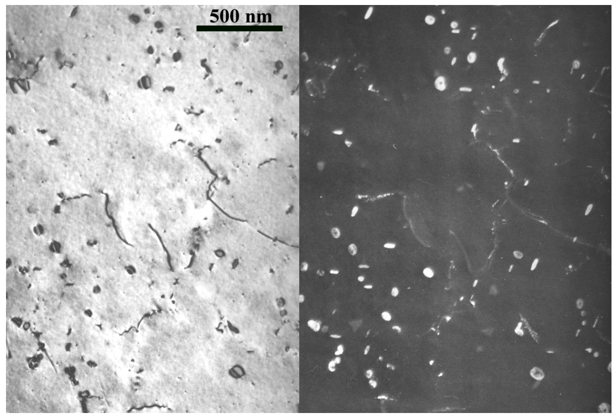
Nucleation and growth of voids

Microchemical evolution

Enhanced precipitation



Radiation induced segregation



Radiation induced precipitation

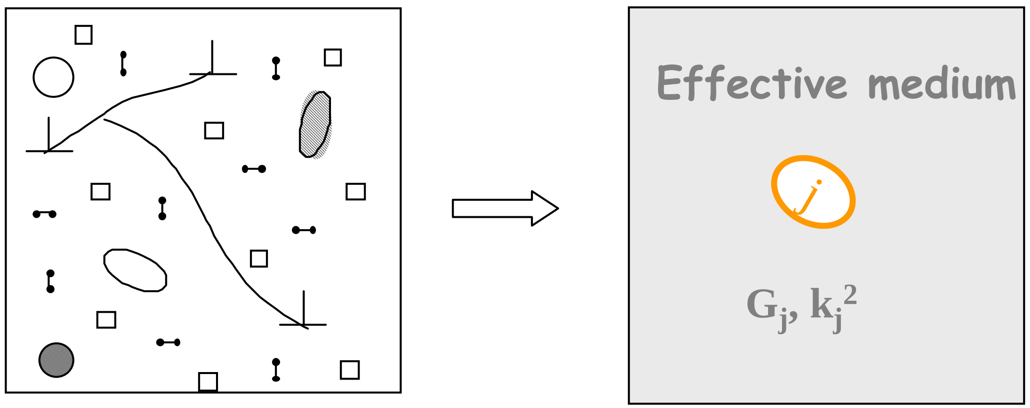
Rate theory basis

• The actual material with its microstructure is replaced by an effective homogeneous medium.

• All processes occur continuously in space and time.

• The evolution of one object embedded in the effective medium is described by an ordinary differential equation (rate theory).

•The number density of objects must be low enough (dilute limit).



Object j embedded in the effective medium.

A simple case : only single point defects evolution

Constant microstructure assumption

creation — recombination — elimination on sink of type p — emission from sink of type p

$$\frac{\partial c_v}{\partial t} = G_v - R\, D_i c_i c_v - \sum_p k^2_{v,p} D_v\, c_v + \sum_p k^2_{v,p} D_v c^e_{v,p}$$

$$\frac{\partial c_i}{\partial t} = G_i - R\, D_i c_i c_v - \sum_p k^2_{i,p} D_i c_i$$

The whole physics is contained in the rate coefficients G, D, k

Rate constant calculations

1. The point defect flux towards the considered sink is calculated by resolving the diffusion equation at stationary state with limit conditions properly chosen.

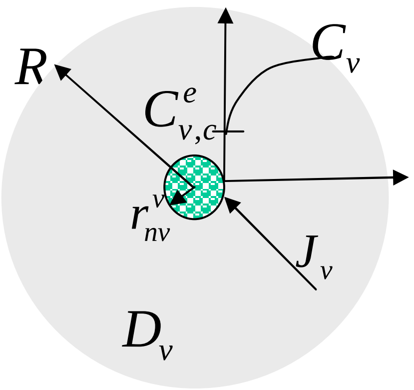
2. Integration over the « surface of the sink ».

3. Multiplication by the « number density » of the considered sinks.

Example: Cavity sink strength

Simplest method

Point defect captured by a voids made of n vacancies :



$$\nabla^2 C_v = 0$$

$$C_v = C^e_{v,c} \quad at \quad r^v_{nv}$$
$$C_v = C_v \quad at \quad R$$

⇨

$$I^{0v}_{nv} = 4\pi r^v_{nv} D_v \left(c_v - c^e_{v,c}\right)$$ r^v_{nv} capture radius

$$I^{0v}_{nv} = I^{0\beta v}_{nv} - I^{0\alpha v}_{nv}$$

absorption (→ $I^{0\beta v}_{nv}$) emission (→ $I^{0\alpha v}_{nv}$)

$$I^{0\beta v}_{nv} = 4\pi r^v_{nv} D_v c_v$$
$$I^{0\alpha v}_{nv} = 4\pi r^v_{nv} D_v c^e_{v,c}$$

Then: $$k^2_{v,nv} = 4\pi r^v_{nv} C_{nv}$$

Where C_{nv} is the number density of cavities containing n vacancies.

Cavity sink strength

Self consistent method (R. Bullough)

Cavity of radius r_{nv}^{v} now embedded in an effective medium in which vacancy are homogeneously created at a rate G_v and that contained sinks for vacancy of sink strength k_v^2 .

$$\nabla^2 C_v - D_v k_v^2 c_v + G_v = 0$$

$$\Downarrow$$

$$k_{v,nv}^2 = 4\pi \, r_{nv}^{v} C_{nv} \boxed{(1 + k_v r_{nv}^{v})}$$

$$\Downarrow$$

Multi-sink correction

often negligible in actual conditions.

Bias coefficient

If interaction energy E_α between the point defect of α type and the object, capture coefficient solution of :

$$\nabla^2 C_\alpha + \frac{1}{kT} \nabla C_\alpha \nabla E_\alpha = 0$$

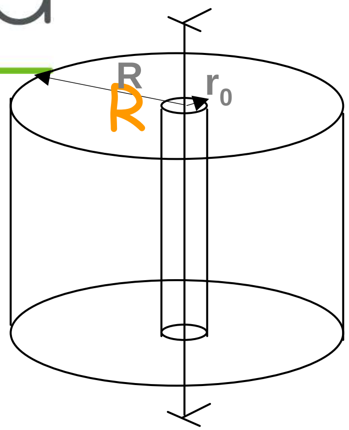
Instead of calculating the interaction energy the interaction very often treated phenomenologically by multiplying the capture radius by a coefficient Z

$$k^2_{\beta,n\alpha} = 4\pi r^{\beta}_{n\alpha} Z^{\beta}_{n\alpha} C_{n\alpha}$$

$Z^{\beta}_{n\alpha}$ bias coefficient of the object . $n\alpha$ for point defects of type β

Dislocations sink strength

$$k^2_{d,\alpha} = Z^{\alpha}_d \rho_d \ ,$$ with ρ_d dislocation density



If no interaction between point defect α and dislocation:

$$Z^{\alpha}_d = \frac{2\pi\rho_d}{\ln(R / r_0)}$$ with $R \cong (\pi\rho_d)^{-1/2}$

If significant interaction:

$$Z^{\alpha}_d = \frac{2\pi\rho_d}{\ln(R / r^{\alpha}_d)} \qquad r^d_{\alpha} = \frac{\mu b(1+\nu)V^r_{\alpha}}{6(1-\nu)\pi kT}$$

with V^r_{α} relaxation volume of the point defect of α type.

- not only proportional to the sink density
- an additional term contains also the sink density = the multi-sink correction.

Often simplified: as the relaxation volume is considerably larger for interstitial than for vacancy $Z^v_d = 1$ and $Z^i_d = 1.1 \ \ or \ \ 1.2$

Grain boundary sink strength

For the point defects of α type

$$k_{gb,\alpha}^{2} = \frac{6k_\alpha}{d}$$

With k_α the total sinks strength of the effective medium for the point defect α

The multi sink effect cannot be ignored for grain boundaries.

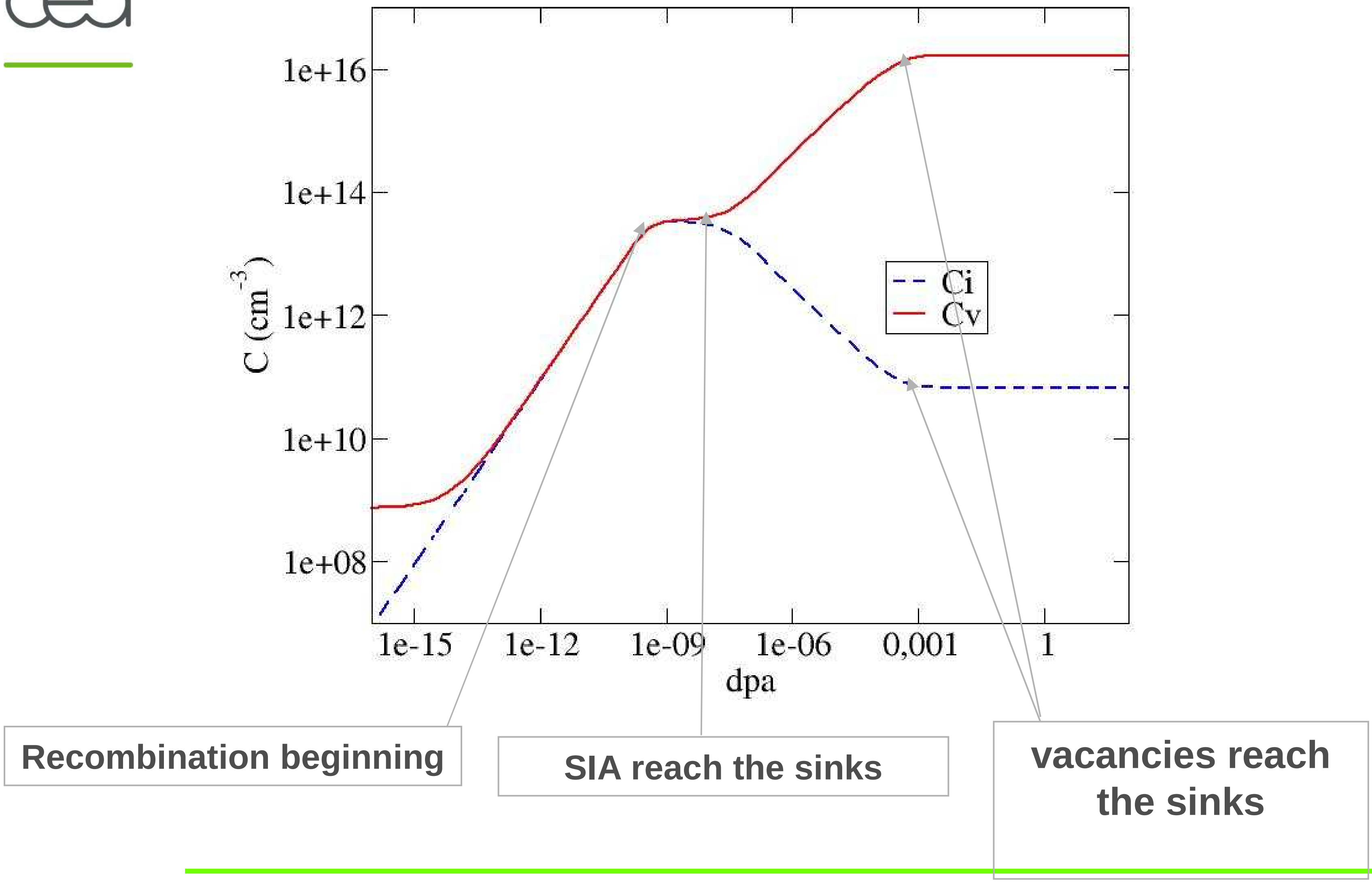
Properties of point defect: reminding

	H_v^f	H_v^m	V_v^r	H_i^f	H_i^m	V_i^r
Ni	1.6	1.1	-.20	≈4.0	0.15	1.8
Fe	1.6 (2.0)	1.3 (0.6)	-.20	≈4.0	0.3	1.1
Zr	>1.35	.7 ?	-.05	?	0.26	.6

Exemples de paramètres caractérisant les DP dans Ni, Fe et Zr.
(Laudolt-Bôrnstein, Wollenberger 1983 et Ehrhart et al 1986).

Calculated single point defect evolution in iron

Iron, 2 10^{-8}dpa/s, 300°C, low dislocation density..



Point defect: stationary state

If $c^{e}_{v,p} << c_v \quad \forall p$

Stationary state satisfies $D_v c_v \sum_p k^2_{v,p} = D_i c_i \sum_p k^2_{i,p}$

Point defect stationary concentrations

- **Sink dominant regime** : $c_v = \dfrac{G}{D_v \sum_p k^2_{v,p}}$ $\quad c_i = \dfrac{G}{D_i \sum_p k^2_{i,p}}$

- **Recombination dominant regime** :

$$c_v = \left(\frac{G \sum_p k^2_{i,p}}{R D_v \sum_p k^2_{v,p}} \right)^{1/2} \qquad c_i = \left(\frac{G D_v \sum_p k^2_{v,p}}{R D_i^2 \sum_p k^2_{i,p}} \right)^{1/2}$$

Growth velocity of point defect clusters at point defect at stationary state

If dislocations are the dominant sinks

Stationary state $$Z_d^v D_v c_v = Z_d^i D_i c_i$$

Growth velocity of a void of radius r_c

$$\frac{dr_c}{dt} = \frac{\Omega}{r_c}\left\{Z_c^v D_v c_v - Z_c^i D_i c_i\right\} \quad \Rightarrow \quad \frac{dr_c}{dt} = \frac{\Omega}{r_c}\frac{Z_d^i - Z_d^v}{Z_d^i} D_v c_v$$

as for void $Z_c^v \approx Z_c^i = 1$

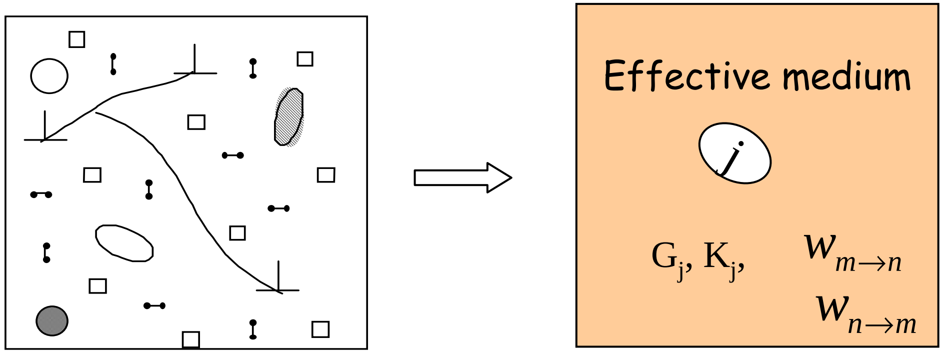
If the mean bias of the medium is the same as bias coefficient for voids (the object we are here interested by):

$$\frac{dr_c}{dt} = 0$$

Rate theory for the clustering of point defects : cluster dynamics

- Based on rate theory
- Gas of clusters embedded in an effective homogeneous medium → Only applicable to diluted object
- Positions of the objects are not considered: (Price to pay to reach large fluences considering a representative volume of materials).

Evolution of the number density of a cluster of j kind



Object j embedded in the effective medium.
(j = nature, size, composition, etc. of the clusters)

$$\frac{dC_n}{dt} = \sum_m J_{m \to n} - \sum_q J_{n \to q} + G_n - K_n C_n$$

In principle able to treat nucleation, growth and coarsening of point defect clusters or precipitates (homogeneous precipitation)

Basic master equation

$$J_{m \to n} = \sum_m w_{m \to n} C_m$$

$$\Downarrow$$

$$\frac{dC_n}{dt} = G_n + \sum_m w_{m \to n} C_m - \sum_q w_{n \to q} C_n - K_n C_n$$

All the physics is contains in the coefficients G(j), w(k,j), K_j

In principle as many equations as kind of cluster j (size,nature)

But N_{max} (cluster sizes) = number of differential equations limited by the ability of computer and by the CPU time.

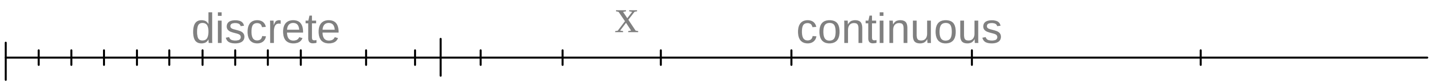
Treatment of large clusters

To reach large cluster sizes (>2nm), two methods:

- Transformation of the discrete general equation into a continuous Fokker-Planck type equation:

$$\frac{\partial C(x)}{dt} = \frac{\partial}{\partial x}\left[f(x)C(x)\right] + \frac{\partial^2}{\partial x^2}\left[d(x)C(x)\right]$$

To solve the continuous equation: Discretizated with Δx increasing with x



New numerical scheme always stable © V. Duwig et al.

Grouping method: a group represented by one element. Golubov (2001)

Distribution characterize only by:

- The first moment of the distribution (conservation of the cluster number)

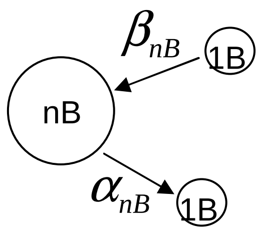
- The second moment of the distribution (matter conservation)

Two times more equations.

A simple case : precipitation in dilute solid solution

- only single B atoms are mobile
- only single B atoms can be emitted from a precipitate
- spherical precipitates of n solute atomes

$$J_{m_B \to n_B} = \beta_{n_B} C_{1_B} C_{n_B} - \alpha_{n_B+1} C_{n_B+1}$$



$$\beta_{n_B} = 4\pi r_{n_B} D_{1_B}$$

$$\alpha_{n_B} = 4\pi r_{n_B-1} \frac{D_1}{\Omega} \exp\left[\left(G_{n_B} - G_{n_B-1} - G_1\right)/kT\right]$$

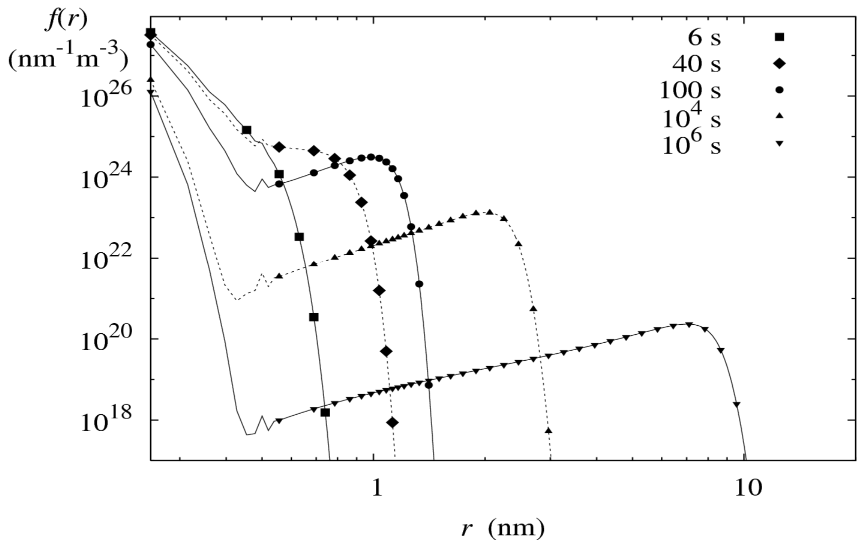
Capillary model

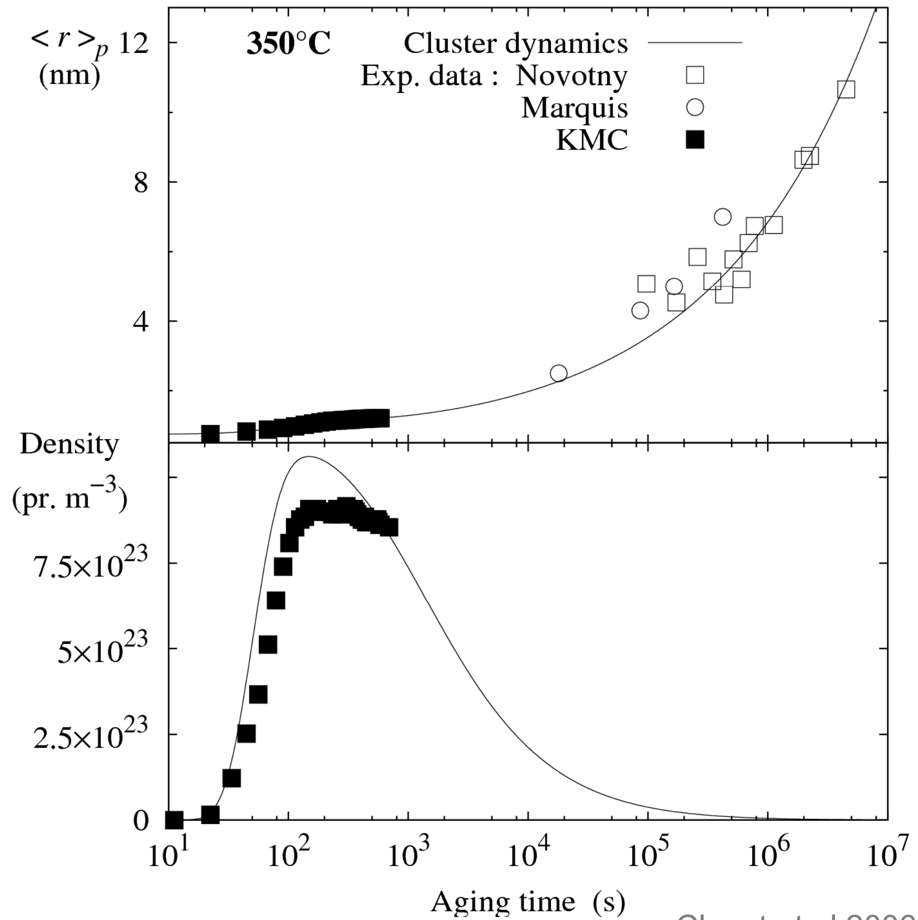
$$G_{n_B} = 2 n_B \mu(C_B^0) + \frac{n_B}{C_p} \Delta G^{nuc}\left(C_B^0\right) + \left(576\pi\Omega^2\right)^{2/3} n_B^{2/3} \sigma_{n_B}$$

$$\alpha_{n_B} = 4\pi r_{n_B-1} \frac{D_1}{\Omega} \exp\left[\left(576\pi\Omega^2\right)^{1/3} \left\{ n_B^{2/3} \sigma_{n_B} - (n_B - 1)\sigma_{n_B-1} - \sigma_{1_B} \right\} / kT\right]$$

α_{n_B} independent of ΔG^{nuc}

Al_3Sc precipitation in AlSc0.18at% solid solution



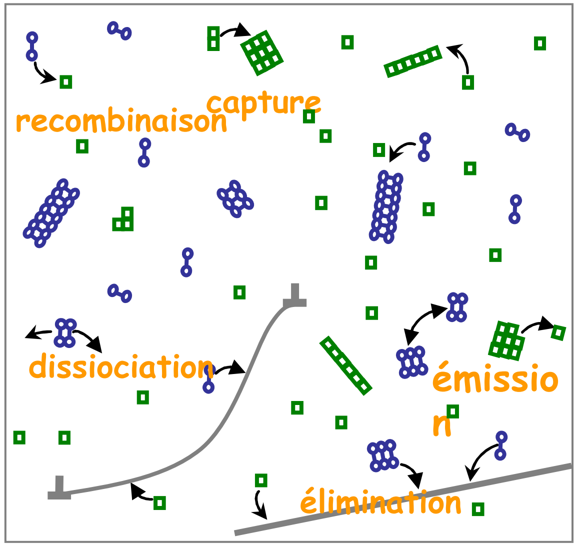


Clouet et al 2006

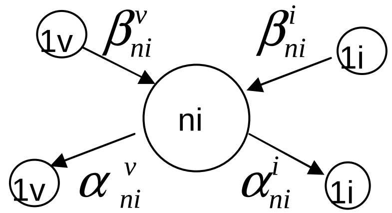
Point defect clustering under irradiation.

Pont defects are not conservative : creation and elimination

OBJECTS
SIA clusters = dislocation loops
Vacancy clusters = dislocation loops, voids, stacking fault tetraedra



Typical ODE in a simple case: only SIA's and vacancies are 3D mobile



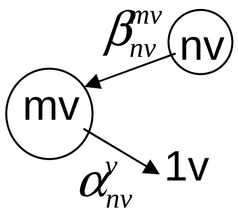
$$\frac{dC_{ni}}{dt} = G_{ni} + \left(\beta^{i}_{(n-1)i} C_{1i}\right) C_{(n-1)i} + \left(\beta^{v}_{(n+1)i} C_{1v} + \alpha^{i}_{(n+1)i}\right) C_{(n+1)i} - \left(\alpha^{i}_{ni} + \beta^{v}_{ni} C_{1v} + \beta^{i}_{ni} C_{1i}\right) C_{ni}$$

$$\frac{dC_{1i}}{dt} = G_{1i} + \beta^{v}_{2i} C_{1v} C_{2i} - C_{1i} \sum_{m=1} \beta^{i}_{mi} C_{mi} - \beta^{i}_{1i} C^{2}_{1i} - C_{1i} \sum_{m=1} \beta^{i}_{mv} C_{mv} - \beta^{v}_{1i} C_{1i} C_{1v} + \sum_{m=2} \alpha^{i}_{mi} C_{mi} + \alpha^{i}_{2i} C_{2i} + \sum_{m=2} \alpha^{i}_{mv} C_{mv} - K_{i} C_{1i}$$

If cluster are 3D mobile, equations simply more complicate

Kinetic coefficient for 3D mobile objects

nv+mv↔(n+m)v



Capture and emission by point defect clusters

$$\beta_{nv}^{mv} = 4\pi r_{nv}^{mv}(D_{nv} + D_{mv})$$

$$\alpha_{nv}^{v} = 4\pi r_{(n-1)v}^{v} D_v \exp(-E_{nv}^{B} / kT)$$

r_{nv}^{mv} = reaction radius ≠ of the actual radius of the objects

If elastic interaction between reacting objects (bias coefficient) in r_{nv}^{mv}

Importants parameters

External : T, G_n

Material:

Mobility : $D_n = D_{n0} \exp(-E_n^m / kT)$

Formation energy of clusters: E_n^f

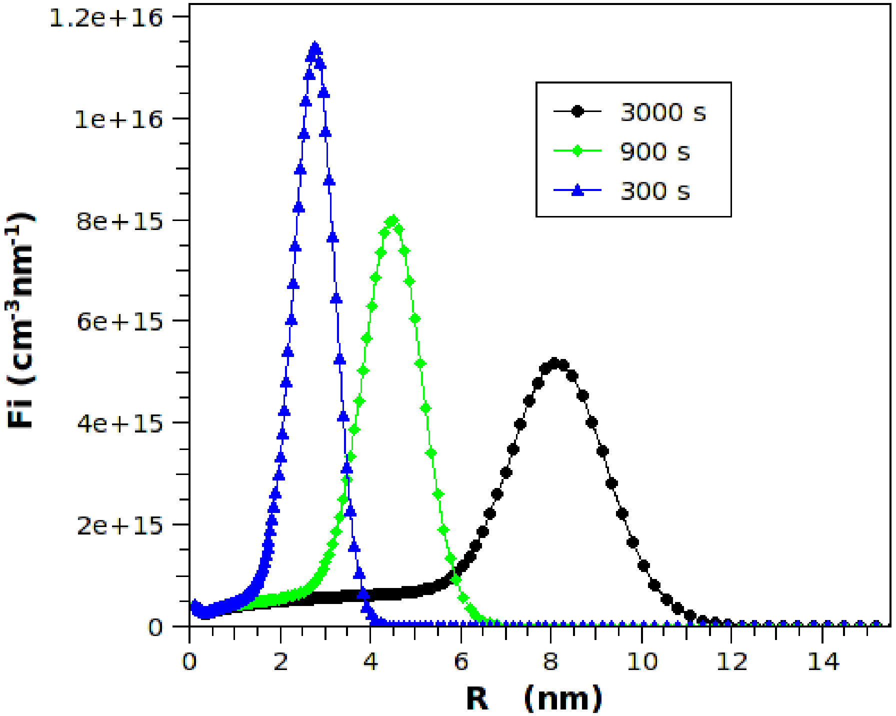
⟺

Further approximation to reduce the number of parameters

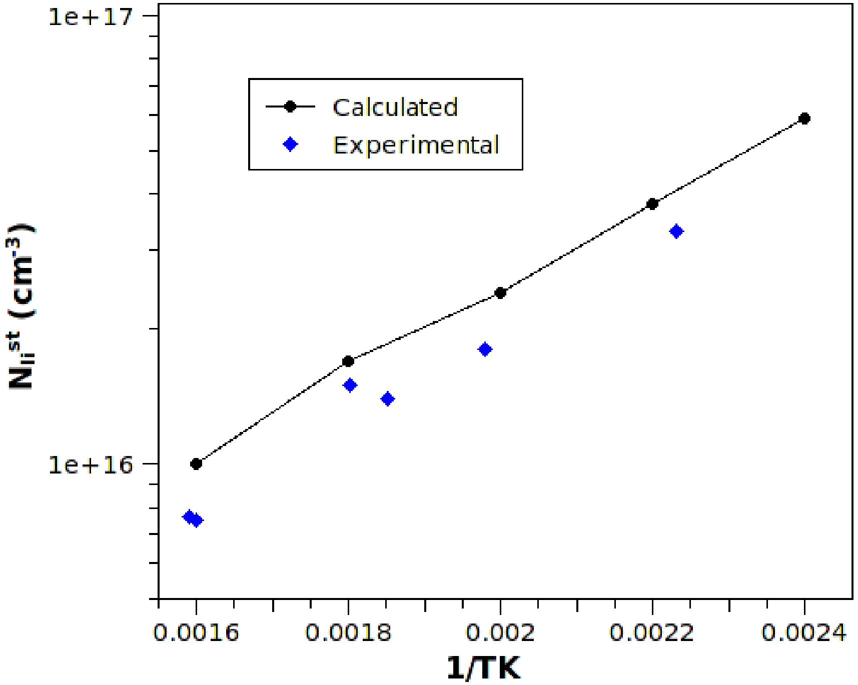
$$E_n^f = \frac{E^f - E_2^B}{2^{2/3} - 1} n^{2/3}$$

Continuous isothermal irradiation.

Point defect clusters in the FeCu 0.1 at% continuously irradiated with 1 MeV electrons.



Interstitial loop distributions



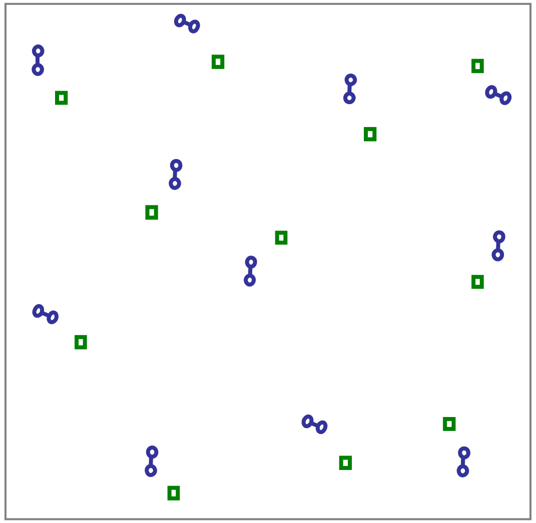
Emi (eV)	EB2i (eV)	Emv (eV)
0.3	1.2	1.36

Only single SIA and single-vacancies mobile.

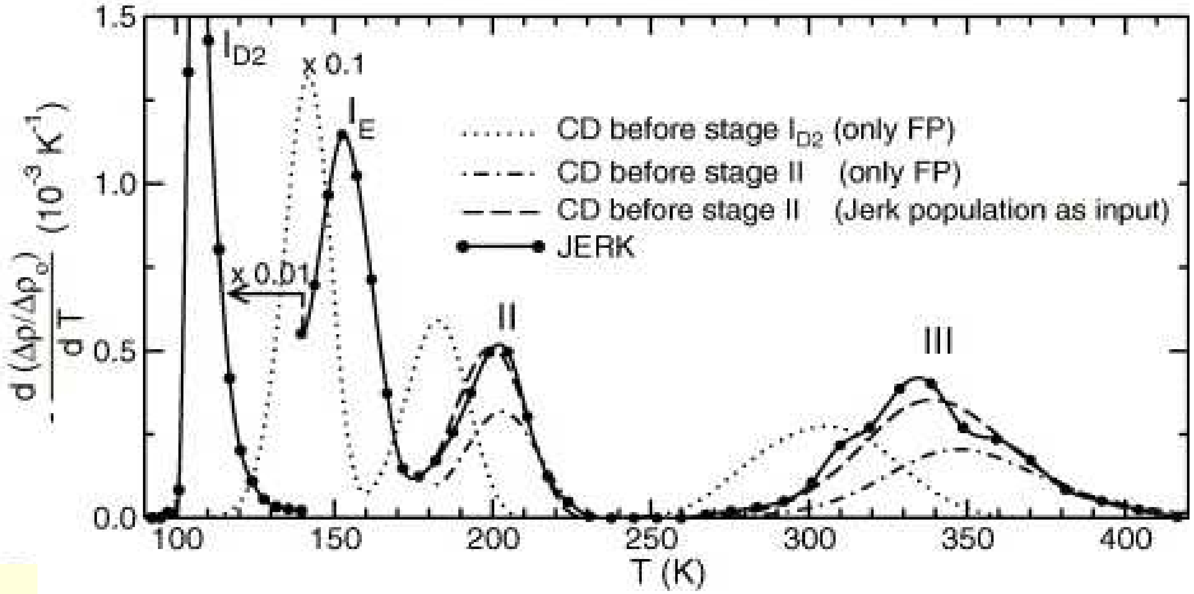
Effect of spatial correlations

A full multi-scale modeling: isochronal recovery of ultra pure Fe electron irradiated at 4K.

Comparison between CD, KMC.



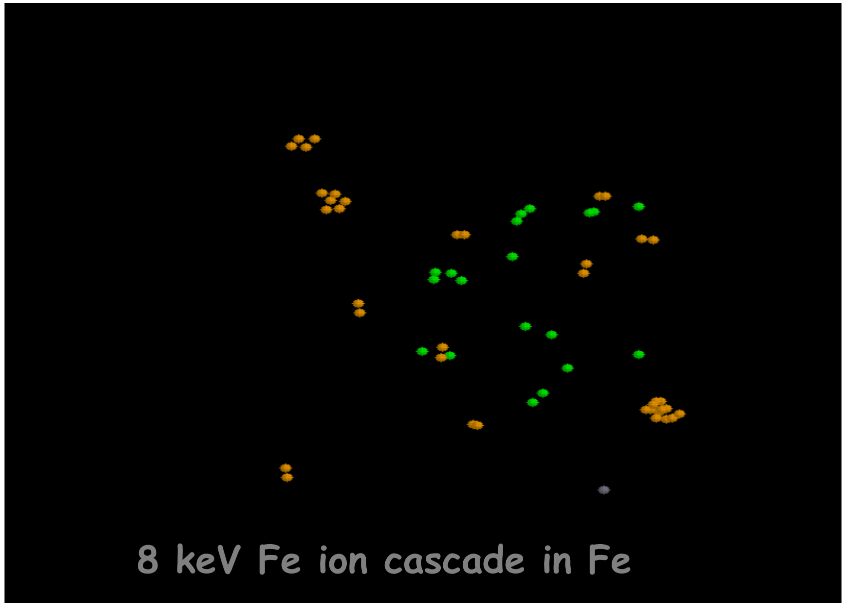
Correlations between vacancies and SIA even under electron irradiation



CD given good results only if a short KMC annealing at stage I is performed to erase correlations.

Displacement cascade correlations

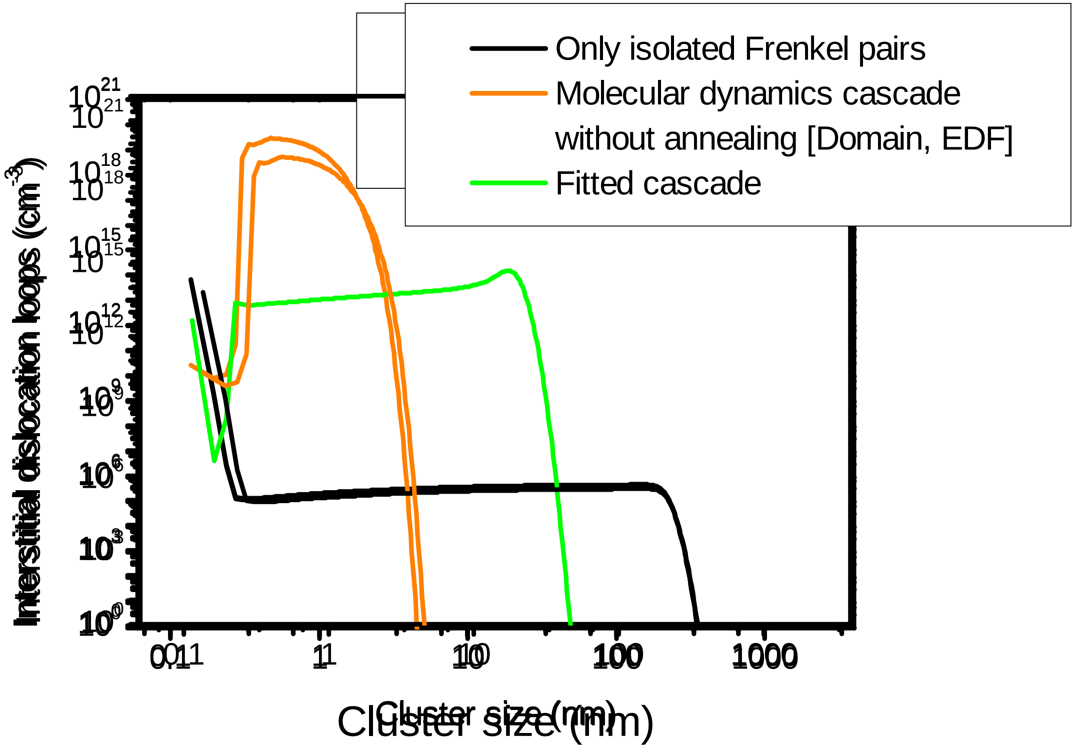
Strong correlations in displacement cascades
(neutron and ion irradiations)



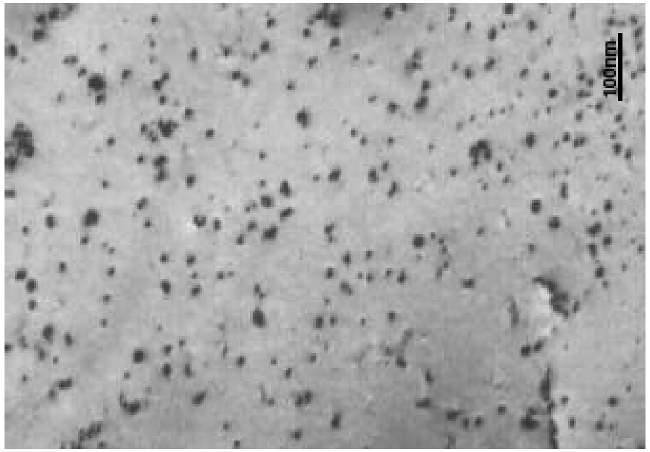
The point defect cluster distribution cannot be directly taken as the point defect sources in RT equations.
Necessity to carried out a KMC pre-annealing of the cascade to minimize the correlations.

Example: point defect clusters in neutron irradiated iron

Parameters for small point defect clusters from ab initio calculations.

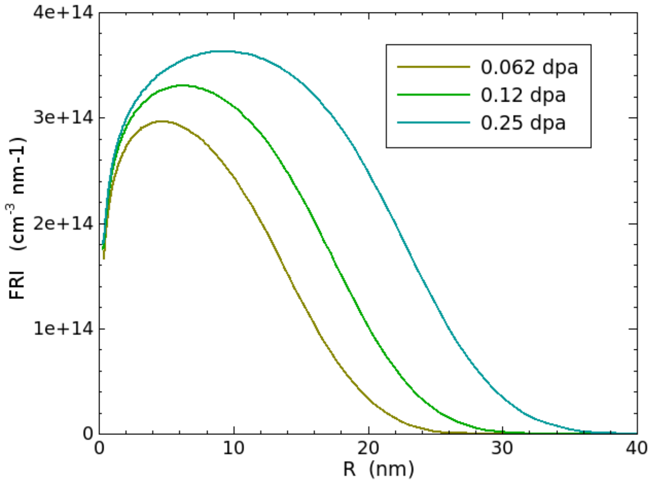


— Only Frenkel pairs
— Molecular dynamics cascades
— Fitted source term on experiments (Kr 2 MeV ions and BR2 neutrons)

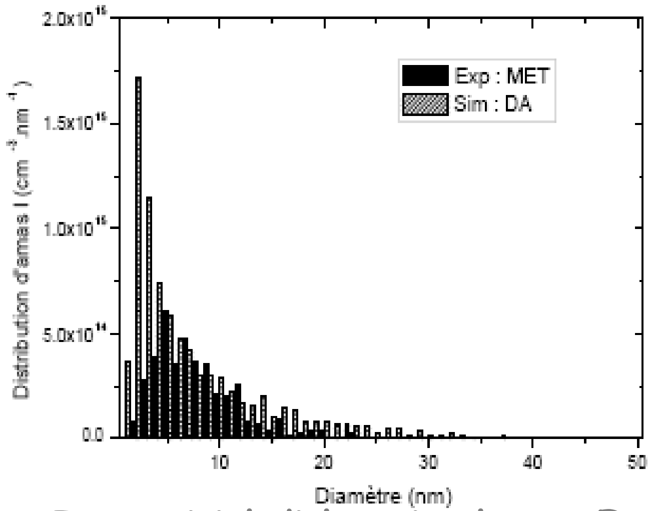


Interstitial dislocation loops, Fe, 300°C,BR2
(M. Hernandez CIEMAT)

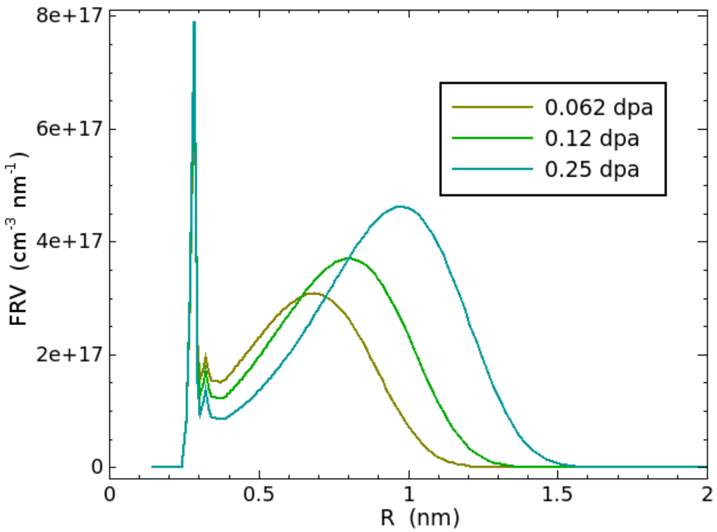
Neutron irradiated iron (2)



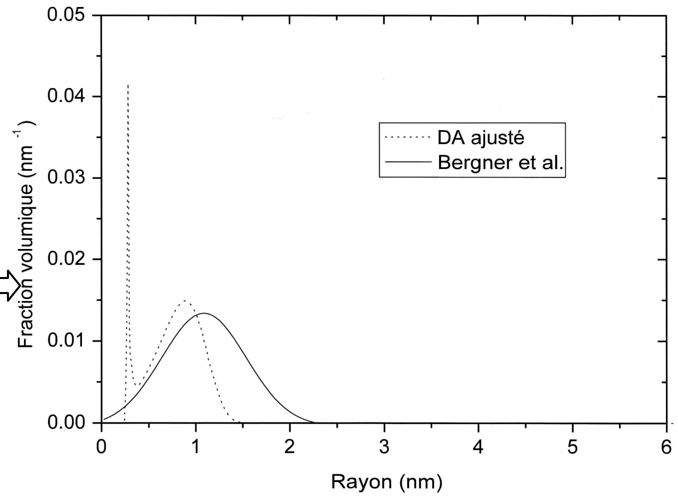
Interstitial loop distribution



Interstitial dislocation loops, Fe, 300°C,BR2



Cavity distribution



Comparison with experimental (SANS) vacancy distribution

Conclusion

- **Cluster dynamics (based on rate equations) modeling remains a very interesting method to simulate the long term evolution of materials.**
- **Low computational cost compared to OKMC**
- **Allows very long time evolution of a representative volume of materials impossible to obtain with KMC.**
- **Being based on an homogenization procedure, care must be taken when spatial correlations are important.**

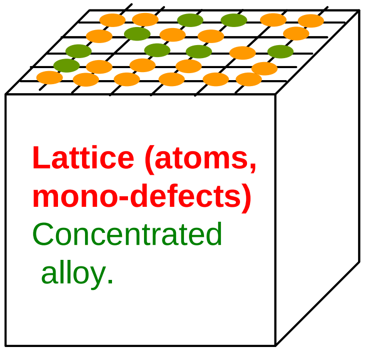
Long term evolution modeling of clusters

← atoms → ← gas of clusters →

MFVIC

Atomic Kinetic Monte Carlo (AKMC)

Microchemical changes



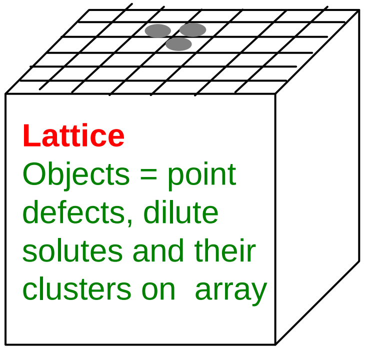
$V \simeq 10^{-4}\ \mu m^3$
$t \simeq 10^{11}$ jumps

- Atom or defect on every lattice site
- **Jump probabilities of atoms**
- Interactions between atoms

Full thermodynamics

Object Kinetic Monte Carlo (OKMC)

Point defect clusters

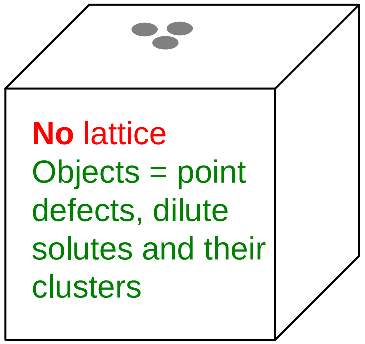


$V \simeq 10^{-4}\ \mu m^3$;
$t \simeq$ limited (T, G dependent)

- Gaz of cluster
- **Jump probabilities of objects**
- ω_α , $E^f_{cluster}$, r_c

Event Kinetic Monte Carlo (EKMC)

Point defect clusters



$V \simeq 10^{-4}\ \mu m^3$;
$t \simeq$ limited (T, G dependent)

- Gaz of cluster
- **Probability of reaction between objects**
- D_α , $E^f_{cluster}$, r_c

Cluster Dynamics (CD) (Rate theory)

Point defect clusters

Rate equations (homogeneous in space and time)
Number density of objects / cm³ (point defects, solutes and their clusters)

V unlimited
t unlimited

- Gaz of cluster
- **Set of ODE**

$$\frac{\partial C_j}{\partial t} = F(C_j, C_k, \ldots)$$

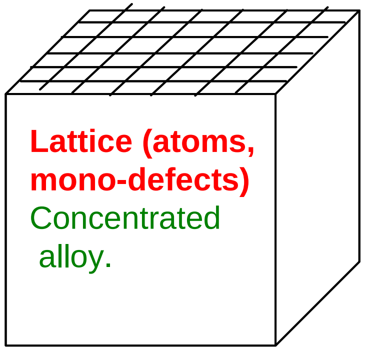
- D_α , $E^f_{cluster}$, r_c

Long term evolution modeling: precipitation, segregation

← atoms → ← gaz of clusters →

Atomic Kinetic Monte Carlo (AKMC)

Microchemical changes



V ≃ 10^{-4} µm^3
t ≃ 10^{11} jumps

- Atom or defect on every lattice site
- **Jump probabilities of atoms**
- Interactions between atoms

Full thermodynamics

Self Consistent Mean Field

Transport coefficients Lij (Microchemical changes)

Lattice (atoms and mono-defects)
Atom embedded in the mean medium.
Concentrated alloy.

- **Jump probabilities of atoms**
- Interactions between atoms

Full thermodynamics

Gaz of clusters

- OKMC
- EKMC
- CD (MFVISC)

Dilute alloys

Transport phenomena and thermodynamics only partially taken into account